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Activation of amorphous bismuth oxide via plasmonic Bi metal for efficient visible-light photocatalysis

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ABSTRACT

Amorphous semiconductors are seldom exploited as effective photocatalysts, as they are restricted by abundant bulk defects as carrier recombination centers. To activate amorphous bismuth oxide for efficient visible-light photocatalytic performance, a novel and facile strategy was developed. Plasmonic Bimetal-decorated amorphous bismuth oxide (Bi–BiO) was prepared by partial reduction with $NaBH_4$. The content of Bi metal and the photocatalytic activity of the catalysts can be modulated by controlling the concentration of $NaBH_4$ solution. Various techniques were employed to explore the structural features, optical properties, and active species during photocatalysis. The as-synthesized Bi–BiO catalysts were applied in photocatalytic removal of NO in air under and exhibited highly enhanced visible light photocatalytic activity. The significantly increased photocatalytic capability can be attributed to the combined effects of the enhanced visible light absorption and the improved separation efficiency of the charge carriers attributed to the surface plasmon resonance conferred by Bi metal. The advanced Bi–BiO catalysts also exhibited high photochemical and structural stability under repeated irradiation. Moreover, in situ DRIFT was carried out to reveal the time-dependent evolution of reaction intermediates during photocatalytic NO oxidation. A molecular-level photocatalysis mechanism was first proposed for Bi–BiO based on ESR and in situ DRIFT. This work could provide a new perspective in utilizing non-noble-metal Bi as a key activation factor to trigger the photocatalytic ability of amorphous semiconductors.

1. Introduction

Photocatalysis is a green technology for environmental remediation and solar energy conversion. The development of efficient visible light photocatalysts that could effectively utilize solar energy is the key to practical application of photocatalytic technology [1–3]. It is well known that the performance of photocatalysts is predominantly determined by the light utilization efficiency and charge separation efficiency [4–8]. Under light irradiation of semiconductors, the photogenerated electrons and holes may recombine by certain routes before they can be involved in the subsequent reactions. To promote charge separation, various strategies have been adopted, such as doping with heteroatoms, formation of heterostructures, and enhancement of crystallinity [9–11].

Recently, amorphous semiconductors have been developed by relatively simple and facile methods [12–17]. However, these amorphous materials are originally disordered, and the short-range order is in general so well defined that abundant bulk defects can occur at the charge recombination centers [18]. Thus, the amorphous semiconductors exhibit limited photocatalytic activity due to a high charge carrier recombination rate. To overcome the drawbacks of amorphous semiconductors, it is essential to enhance the crystallinity and reduce the number of bulk defects. For instance, Amano et al. found that amorphous Bi_2WO_6 showed little photocatalytic activity [19]. Subsequently, they applied hydrothermal treatment to improve the crystallinity of amorphous Bi_2WO_6, and enhanced photocatalytic activity was achieved due to promoted charge separation [19]. Xiao and co-workers employed thermal calcination for amorphous bismuth oxide with low photocatalytic performance to obtain α-Bi_2O_3 and β-Bi_2O_3 with excellent photocatalytic activity under visible light irradiation [20]. However, the approaches to enhancing the crystallinity of

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semiconductors usually involve high-temperature or high-pressure treatment.

Bismuth as a semimetal has attracted great interest, as it has unique properties, such as a very small effective mass, a large mean free path, a long Fermi wavelength, high carrier motilities, and small band overlap energy [21–25]. Recently, low-cost Bi metal has been found to exhibit surface plasmon resonance (SPR), allowing it to achieve the function of noble metals (Au, Ag, etc.) in a similar way [25,26]. With the significant advantages of Bi metal, it has been widely applied to enhance the photocatalysis of other semiconductors as a plasmonic co-catalyst. For example, Bi/$(BiO)_2CO_3$ [27], Bi/g-C_3N_4 [28], Bi/TiO_2 [29], and Bi/BiOCl [30] have been developed and have exhibited upgraded photocatalytic performance in comparison with their individual components by virtue of the metal Bi, which can promote charge separation through SPR. On the other hand, bismuth oxide has five polymorphic forms: α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (body-centered cubic), δ-Bi_2O_3 (cubic), and ε-Bi_2O_3 (triclinic) [31]. Among these polymorphic forms, β-Bi_2O_3 has a suitable band gap (~2.4 eV), and demonstrates decent photocatalytic performance in comparison with the other phases [31–33]. However, the amorphous bismuth oxide normally exhibits poor photocatalytic performance. The photocatalytic activity would be promoted if the crystallinity of amorphous bismuth oxide could be enhanced to form β-phase Bi_2O_3 [34]. To the best of our knowledge, the utilization of the SPR effects of Bi metal to activate amorphous bismuth oxide has never been reported. Also, there have been few studies on facile ways to activate the amorphous structure with limited activity.

In the present work, amorphous bismuth oxide (A-BiO) was prepared by a facile method. The A-BiO sample showed almost no activity, due to the high charge carrier recombination rate. To activate the amorphous bismuth oxide, a facile partial reduction method is developed to generate Bi metal in situ on amorphous bismuth oxide with sodium borohydride as the reductant. The as-prepared Bi–BiO nanohybrids were applied for photocatalytic removal of low-concentration NO in air under visible light illumination and showed dramatically enhanced activity because of SPR, enhanced visible light absorption, and accelerated electron–hole pair separation induced by the Bi nanoparticles. The relationship between amount of coupled Bi metal and photocatalytic performance was also revealed. The function of Bi nanoparticles as a co-catalyst is similar to that of noble metals. Significantly, the Bi–BiO samples also exhibited excellent photochemical stability, which will pave the way to a new approach for substituting the inexpensive base metal for the precious noble metals to activate the amorphous semiconductor photocatalyst for practical applications. Moreover, the photocatalytic NO oxidation process over Bi–BiO catalysts was monitored for the first time using in situ DRIFT, offering a powerful new method to investigate the gas-phase photocatalytic reaction mechanism.

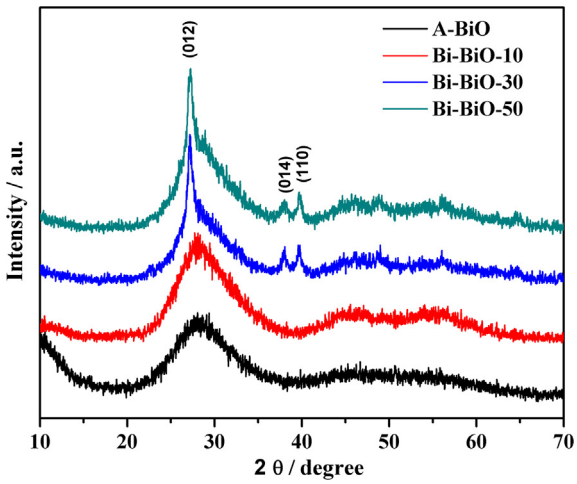

Fig. 2. XRD patterns of all samples.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of amorphous bismuth oxide (A-BiO)

In a typical procedure, $Bi(NO_3)_3{\cdot}5H_2O$ (2.91 g, 6 mmol) was dissolved in a mixed solution that contained glycerol (30 mL) and absolute ethanol (30 mL). Then the mixture was treated with vigorous stirring and ultrasonic dispersion to form a homogeneous solution. The obtained solution was transferred into a Teflon-lined stainless steel autoclave (100 mL), sealed, and heated at 160 °C for 3 h. After cooling to room temperature, the as-formed precipitate was collected and washed several times with deionized water and absolute ethanol, followed by drying at 60 °C.

2.1.2. Synthesis of Bi-metal-decorated amorphous bismuth oxide (Bi-BiO)

A quantity of 1.0 mmol of the A-BiO was added into 100 mL of deionized water containing 1.0 g PVP. A certain concentration of $NaBH_4$ (30 mL) was added dropwise into the suspension, stirred for 1 h, and then aged for 1 h. The resulting precipitates were gathered, rinsed four times with ethanol and deionized water, and dried at 60 °C in air. The concentration of $NaBH_4$ is controlled at 10, 30, and 50 mmol/L, and the obtained samples were denoted as Bi-BiO-10, Bi-BiO-30, and Bi-BiO-50, respectively.

2.2. Characterization

The crystal phases of the sample were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (Model D/max RA, Rigaku Co., Japan). Scanning electron microscopy (SEM, Model JSM-6490,

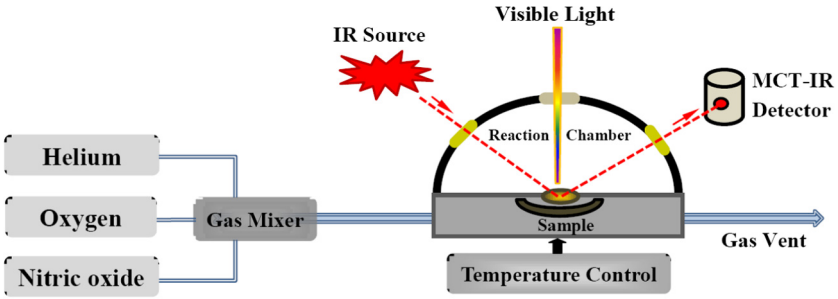

Fig. 1. Schematic diagram the of in situ DRIFT reactor system.